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General implementation of the relativistic coupled-cluster method

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We report the development of a general order relativistic coupled-cluster (CC) code. Our implementation is based on Kramers-paired molecular spinors, utilizes double group symmetry, and is applicable with the full Dirac–Coulomb and several approximate relativistic Hamiltonians. The available methods include iterative and perturbative single-reference CC approaches with arbitrary excitations as well as a state-selective multi-reference CC ansatz. To illustrate the performance of the new code, benchmark calculations have been performed for the total energies, bond lengths, and vibrational frequencies of the monoxides of Group IVa elements. The trends due to the simultaneous inclusion of relativity as well as higher-order electron correlation effects are analyzed. The newly developed code significantly widens the scope of the *ab initio* relativistic calculations, for both molecules and atoms alike, surpassing the accuracy and reliability of the currently available implementations in the literature. © *2010 American Institute of Physics*. [doi:10.1063/1.3518712]

I. INTRODUCTION

The development of relativistic theories to molecular systems has been an important thrust in the field of quantum chemistry over the years (for a recent review see, e.g., Ref. 1). A fully relativistic formalism would be symmetric with respect to both positive (electronic) and negative (positronic) energy states and intrinsically requires a four-component description of the wave function. Since applications in physics and chemistry below the sub-MeV energy scales hardly involve the positronic degrees of freedom, however, it usually suffices to make the so-called no-pair approximation and exclude those degrees of freedom at some stage in the calculations. This is often done prior to the determination of molecular orbitals and combined with a neglect of picture change in the two-electron interaction to reduce computational costs. A more rigorous but also more costly alternative is to first determine four-component molecular orbitals and only invoke the no-pair approximation when treating electron correlation. In both cases one finally obtains an effective two-component description of the wave function in which only the electronic degrees of freedom are accounted for. With several ways[2–9] to transform the four-component Dirac Hamiltonian into two-component Hamiltonians and the possibility to treat the spin-free (scalar relativistic) and the spin-dependent (spin-orbit coupled) relativistic effects separately,[10] a large number of both two- and four-component relativistic approximations have been proposed and implemented. Nevertheless, practical applications of two- or four-component calculations that include spin-orbit coupling from the start are still rather scarce, particularly for large molecules, as this leads to algorithms that are an order of magnitude more costly than the standard algorithms of quantum chemistry.

Although, the Dirac–Hartree–Fock Hamiltonian augmented with the two-electron Coulomb and Breit or Gaunt interaction terms takes into account the relativistic effects quite comprehensively, considering the electron correlation effects together with the relativistic effects on an equal footing is indispensable for reliable description of the electronic structures and spectroscopic properties of the molecules containing heavier atoms. However, due to the computational costs of treating both effects many of the published calculations treat either the relativistic effects or the correlation effects, quite often both, only approximately.

The relativistic correlation methods reported in the literature include the Kramers-restricted closed shell CC theory with single and double excitations (CCSD),[11] Kramers-unrestricted open-shell CCSD theory with partial triple excitations [CCSD(T)],[12] and the multi-reference Fock-space CCSD(T) theory[13]; all three in conjunction with the two- and four-component Dirac–Coulomb–(Gaunt) reference wave functions by Visscher *et al.*, the two-component CCSD and CCSD(T) implementation using effective core potentials by Lee *et al.*,[14] the valence universal Fock-space CC methods developed for atoms by Eliav *et al.*,[15,16] by Chaudhuri *et al.*,[17,18] the configuration interaction (CI) method with a generalized active space concept built over the Kramers-restricted multi-configuration self-consistent-field (KR-MCSCF) reference wave function by Fleig *et al.*,[19–22] the second-order Møller–Plesset perturbation theory,[23–25] the generalized multi-configurational quasi-degenerate perturbation theory (MCQPT) by Miyajima *et al.*,[26] the complete active-space second-order perturbation theory with the Dirac–Coulomb Hamiltonian (DC-CASPT2) by Abe *et al.*,[27] relativistic density functional theory (DFT) by Liu *et al.*,[28] independently by Hirao *et al.*,[29] Saue and Helgaker,[30] and Quiney *et al.*,[31–34] the time-dependent DFT for excitation energies developed by Liu and co-workers[35–38] and Saue and co-workers,[39] the

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relativistic quantum Monte Carlo (QMC) method using the zeroth-order regular approximation (ZORA) by Nakatsuka *et al.*[40] Very recently a two-component closed-shell CCSD(T) approach using the relativistic effective core potentials with spin-orbit coupling included in the post-Hartree–Fock step[41] and the application of direct perturbation theory (DPT) to compute the relativistic corrections to some electrical properties of third and fourth row molecules[42] have been reported by Gauss and co-workers. Thus, a variety of post-HF/DF methods are developed over either quasi- or full-relativistic Hamiltonians. So far, however, not much attention has been paid to the treatment of higher-order correlation effects.

The comprehensive treatment of the electron correlation effects requires methods beyond those generally applied: DFT, finite-order MBPT, restricted CI, truncated CC methods. Most of the molecular applications such as equilibrium geometries, vibrational frequencies, transition properties, etc., however, demand the inclusion of higher-order excitations, in particular, the quadruple excitations[43–45] if high accuracy is needed. Nonetheless, the prohibitive scaling of the full CC/CI methods and the associated high computational costs make them impractical for the application to heavier systems. Therefore, the development of more efficient approximate many-body methods based on the CC formalism are very desirable and timely.

The successful attempts made in the past in this direction include the automated string-based techniques combined with the diagrammatic many-body perturbation theory developed by one of us in the last decade,[45–50] which solve for the arbitrary high excitations in CC and CI methods. The general implementation of CC programs has also been developed by Hirata and co-workers[51–54] using computerized symbolic algebra called tensor contraction engine and string-based automated program generation techniques by Olsen and co-workers.[55] The relativistic extensions of the general order relativistic CC codes, known to our knowledge, are those reported recently by Hirata *et al.*[56] available in the UTChem package[57] and by Fleig *et al.*[58] Although, the implementation in Ref. 56 offers a wide range of correlation methods to be used with the relativistic reference wave function, their relativistic treatment has several intrinsic limitations as it includes corrections only due to relativistic effective core potentials (RECPs) and spin-orbit couplings. Thus, their inclusion of relativistic effects is not as rigorous and complete as in the present work. The implementation in Ref. 58 highlights on the state-specific multireference CC implementation generalized to four-component relativistic formalism. However, the computational scaling of their method is $n_o^{n+2} n_v^{n+2}$ as against the conventional CC scaling of $n_o^n n_v^{n+2}$, where n is the highest excitation and n_o and n_v are the number of occupied and virtual orbitals, respectively. The expensive scaling, therefore, limits the efficiency of their program while handling more than 12 correlated electrons and basis sets of size larger than triple-zeta quality. In contrast, our single- and state-specific multi-reference relativistic CC implementation has an optimal scaling and offers flexibility in the choice of the available methods which include not only the iterative CC and CI methods generalized to arbitrary levels of excitations but also general order perturbative CC methods.

In the current paper, we discuss the modifications required for the conversion of the general order nonrelativistic MRCC program developed by Kállay and co-workers[59] to handle the two- and four-component relativistic Hamiltonians. We also would like to announce the newly developed interface which couples the relativistic version of the MRCC suite[59] with the local version of the relativistic quantum chemistry program suite DIRAC.[60] These two program packages together have a great potential in handling the relativistic effects, both scalar relativistic and spin-orbit effects, together with the correlation effects to arbitrary levels of higher-order excitations. This, therefore, widens the scope of the high precision relativistic correlation calculations and provides the highest levels of accuracy for both molecules and atoms alike, in the future.

In order to demonstrate the capabilities of the newly developed relativistic CC code, we have chosen to study the relativistic contributions and the convergence trends of the correlation effects in the diatomic oxides of Group IVa elements. Although, the considered monoxides have long been the subjects of relativistic and correlation studies, not much work has been done on the spectroscopic properties of these molecules. Various theoretical investigations have only looked in to the electric dipole moment of the heavier molecules. The dipole moment of PbO has been calculated using pseudo-potentials in conjunction with core-polarization potentials and spin-orbit terms.[61] The dipole moments of oxides and sulphides of Pb and Sn have been computed using the nonrelativistic Hamiltonian with the mass velocity and Darwin terms (MVD)[62] and also using the Douglas–Kroll approximation[63] by Kellö *et al.* The scalar Douglas–Kroll approximation up to fifth order in the external potential has been employed in the study of various spectroscopic parameters of SnO.[64] Geometries and dipole moments of the Group IVa monoxides such as GeO, SnO, and PbO have been studied by Dyall using various relativistic and nonrelativistic Hamiltonians[65] at the uncorrelated level of the theory. The essence of most of these and similar calculations on interhalogens,[66] dihalogens,[67] hydrogen halides[68] is that the scalar relativistic methods in which the spin-orbit corrections are ignored can be quite inadequate, and also the simultaneous treatment of both relativistic and correlation effects are necessary in order to produce accurate results. Thus, the reliability of the results of most of these approximate methods needs necessarily be questioned even if they agree with the experimental results. We, therefore, have systematically studied the convergence patterns of the results with respect to the correlation as well as the relativistic effects. The comparative study of the relativistic and nonrelativistic results for the entire series of light through heavy molecules provides crucial insights for understanding the progressive importance of the relativistic effects with respect to the increase in the atomic number especially when high accuracies are aimed for. These are the first calculations to the best of our knowledge where the full relativistic effects through the Dirac–Coulomb Hamiltonian at the SCF level and the higher-order correlation effects including excitations up to quadruples in the post-SCF calculations are considered for these set of molecules.

II. THEORY AND IMPLEMENTATION

The starting point of our general order relativistic CC implementation is the string-based many-body code developed by Kállay and co-workers[45,47,59,69] as well as the relativistic CCSD and CCSD(T) methods of Visscher *et al.*[11,12] as implemented in the DIRAC suite of quantum chemistry programs.[60]

The specialty of the string-based technique is the use of strings of spin-orbital indices rather than the indices for addressing of the wave function parameters, integrals, and intermediates.[45] In the nonrelativistic case strings are ordered sets of spin-orbital indices written as

$$\mathcal{P} = p_1\, p_2\, p_3 \cdots \qquad (p_1 < p_2 < p_3 < \cdots). \tag{1}$$

Relying on this definition cluster amplitudes can be expressed as two index quantities for arbitrary excitation levels and written as $t_{\mathcal{I}}^{\mathcal{A}}$ where $\mathcal{A}$ and $\mathcal{I}$ are the strings of virtual and occupied spin-orbitals, respectively. Similarly, molecular orbital (MO) integrals and intermediates are treated as four-index tensors in the form of $W_{\mathcal{K}\mathcal{I}}^{\mathcal{C}\mathcal{A}}$ where $\mathcal{A}$ and $\mathcal{I}$ are the strings of virtual and occupied fixed spin-orbitals (i.e., orbital labels determined by the projecting determinants in the equations), and $\mathcal{C}$ and $\mathcal{K}$ are the strings of virtual and occupied free labels (i.e., indices which are summed over when calculating the corresponding matrix elements). For the manipulation of quantities stored in terms of strings as well as for the derivation of the working equations automated tools have been elaborated, which highly facilitate the implementation of many-body methods in a general way, independently of the excitation rank of the determinants included in the wave function. In the following we discuss the modifications required to enable relativistic calculations with our code.

Our relativistic implementation follows the lines put forward by Visscher[11,12,70] for the CCSD and CCSD(T) methods. We invoke the no-pair approximation to simplify our Hamiltonian which intrinsically includes the spin-orbit coupling. We also presume that the MOs are Kramers-paired and transform according to the irreducible representations (irreps) of the corresponding double groups. However, we do not impose any time-reversal restriction on the cluster amplitudes. Consequently we should refer to this approach as Kramers-unrestricted relativistic CC method, though this terminology is somewhat misleading since for a closed-shell system the wave function has the correct time-reversal symmetry. The Kramers adaptation of the CC method for the general case (see the recent paper by Fleig[71]), which is closely related to the spin-adaptation problem of the nonrelativistic theory, is not a trivial task and not considered in this publication.

In the relativistic case the spin-orbitals are replaced by spinors, but the basic ideas of the string-based technique are obviously valid for the strings of spinor indices as well. Consequently the fundamental structure of the code is not affected, only some minor modifications are necessary. First, one requires the transformed MO integrals of the relativistic Hamiltonian employed and in order to meet that purpose our code has been interfaced to the DIRAC package,[60] which allows us to use a wide variety of relativistic Hamiltonians. Second, one should take into account the decreased permutational symmetry of the integrals. In the nonrelativistic quantum chemistry—provided that no external magnetic field is applied—the MOs are real and thus the two-electron integrals have eight-fold permutational symmetry. In the relativistic case the orbitals are complex, and even if the integrals can be made real, two symmetries will be lost, and hence only a fourfold symmetry can be utilized. Since, in our code, the formulas are derived and evaluated in terms of antisymmetrized two-electron integrals, which only have the fourfold permutational symmetry by construction, this change do not seriously affect our implementation. In practice the CC code does not need to be changed, only the integral sort algorithm constructing the integral lists of the normal-ordered Hamiltonian (see, e.g., Ref. 45) requires some modifications. Third, one should consider the lack of spin integration. For the nonrelativistic MOs the spatial and spin functions can be separated, and hence during the calculation of the corresponding integrals the spatial and spin integrations can be performed independently. Consequently only certain integrals with a definite number of alpha and beta indices survive. For Hamiltonians containing the spin-orbit interaction this favorable property is lost, and in the general case all the combinations of spinor indices are allowed. Thanks to our flexible tools the appearance of the new integral lists only implies the modification of the integral sort code again, but the CC codes remain intact since the corresponding new terms in the equations are automatically generated and no modification to the CC code is necessary. At last, an important difference in the relativistic case is that the symmetry group of the Hamiltonian is not a point group like in the nonrelativistic case but its double group,[72] hence the use of double group theory is needed if the costs of the calculations are intended to be decreased. While the implementation of the former three points mentioned above is rather technical but straightforward and does not require extensive changes to our CC code, however the double-group symmetry adaptation deserves somewhat more attention.

The notable difference between the double groups and the conventional point groups used in the nonrelativistic quantum chemistry is the existence of a new symmetry operation, the rotation by 2π.[72] As a consequence new types of representation, the so-called fermion irreps appear, and the spinors always transform according to these irreps. The double-group adaptation of our code has been carried out relying on the ideas of Visscher.[12,70] We use spinors that are symmetry functions of the largest Abelian subgroup of the double group of the molecule. As it was demonstrated[70] these groups have the favorable property that the integrals and consequently, all other quantities in a correlation calculation can be made real, which results in a factor of 4 reduction in the scaling of the method. The aforementioned double groups have one-dimensional fermion irreps which are related by complex conjugation. If the spinors are Kramers-paired, the time-reversed conjugate of a function belonging to an irrep transforms according to its complex conjugate irrep.

On the one hand, the transition from conventional point groups to double groups necessitates the replacement of the group multiplication tables used in nonrelativistic codes by those for the double groups. On the other hand, special attention must be paid to the complex valued irreps of double groups. Because of the complex irreps—in contrast to the real

irreps of the nonrelativistic theory—particular attention has to be paid on whether a spinor is used in a bra- or a ket-state. Thus, when determining the symmetry of any quantity, the complex conjugate of the irreps for the spinors used in the bra-function must be considered. For instance, a two electron integral $\langle pq|rs\rangle$ belongs to the irrep $\Gamma_p^* \otimes \Gamma_q^* \otimes \Gamma_r \otimes \Gamma_s$, where p, q, r, and s denote spinors, Γ_p is the irrep for spinor p, and the asterisk refers to complex conjugation. As cluster amplitudes are the matrix elements of the cluster operator, here the virtual indices of the amplitudes stem from the bra state, the corresponding irreps have to be conjugated. In general, for all indices associated with the virtual quasi-creation operators as well as the occupied quasi-annihilation operators the complex conjugate irreps must be considered.

In our string-based technique all the quantities are expressed in terms of strings, and the symmetry of a quantity is given by the direct product of the irreps of the strings. The irrep for a string defined by Eq. (1) can be calculated as

$$\Gamma_{\mathcal{P}} = \Gamma_{p_1} \otimes \Gamma_{p_2} \otimes \Gamma_{p_3} \otimes \cdots. \tag{2}$$

According to the above rules the $t_{\mathcal{I}}^{\mathcal{A}}$ cluster amplitudes have to satisfy the following condition to be nonzero:

$$\Gamma_{\mathcal{A}}^* \otimes \Gamma_{\mathcal{I}} = \Gamma_1, \tag{3}$$

where Γ_1 is the totally symmetric irrep of the double group. For an intermediate $W_{\mathcal{K}\mathcal{I}}^{\mathcal{C}\mathcal{A}}$ the following restriction applies:

$$\Gamma_{\mathcal{C}} \otimes \Gamma_{\mathcal{K}}^* \otimes \Gamma_{\mathcal{A}}^* \otimes \Gamma_{\mathcal{I}} = \Gamma_1. \tag{4}$$

In order to satisfy Eqs. (3) and (4) two important changes have been made. First, in our code, the cluster amplitudes and intermediates are stored in a symmetry-blocked structure, i.e., the elements of the tensors are grouped into blocks according to the irreps of the indexing strings. The addressing of these quantities has been reorganized, and the routines calculating the block addresses have been rewritten to conform to the above equations. Second, all the routines that manipulate cluster amplitudes and intermediates, that is, perform the transposition or the contraction thereof have been modified. As discussed in Ref. 45, in our algorithms each loop running over strings is preceded by another loop over the corresponding irrep, and the latter are restricted to ensure that only nonvanishing elements are treated. This loop structure has been modified to satisfy the new criterion, viz. Eqs. (3) and (4).

The aforementioned changes have been implemented for both iterative and perturbative CC approaches. Currently the following methods are available with relativistic Hamiltonians: iterative single-reference CC approaches including arbitrary excitations (i.e., CCSD, CCSDT, CCSDTQ,...); iterative multireference CC approaches for arbitrary complete active spaces and excitation levels using the state-selective ansatz of Adamowicz and co-workers;[47,73,74] several perturbative single-reference CC approximations for arbitrary excitation levels proposed in Refs. 69 and 75 (including CCSD[T], CCSDT[Q], CCSDTQ[P],...; CCSD(T), CCSDT(Q), CCSDTQ(P),...; CCSDT-1a, CCSDTQ-1a, CCSDTQP-1a,...; CCSDT-1b, CCSDTQ-1b, CCSDTQP-1b,...; CCSDT-3, CCSDTQ-3, CCSDTQP-3,...). It is pertinent to mention that the latter perturbative approximations require a special treatment for open-shell systems if restricted orbitals are used. As it was pointed out in the nonrelativistic case[75–77] the conventional restricted open-shell Hartree–Fock (ROHF) orbitals do not diagonalize the Fock-matrix, and thus make the choice of the zeroth-order Hamiltonian ambiguous. To remedy this problem the use of semi-canonical orbitals was suggested, which diagonalize the occupied–occupied and virtual–virtual block of the Fock-matrix and enable a consistent perturbation treatment. Translating this to the relativistic language would imply the transformation of Kramers pairs to an unrestricted basis and destroy several favorable symmetry properties of the Kramers-restricted formalism. Therefore, in line with Visscher's relativistic CCSD(T) method[12] we propose to go with Kramers-paired orbitals and employ the formulas derived for the semi-canonical ones. Although we know that this approximation is not entirely satisfactory from the perturbation theoretical point of view, it yields however an error which is acceptable.

Concerning the treatment of relativity our program works with several relativistic Hamiltonians implemented in the DIRAC suite[60] including the Dirac–Coulomb, ZORA,[78–80] the Douglas–Kroll,[81] and the exact two-component (X2C)[82,83] Hamiltonians.

It is worth mentioning that besides various CC methods listed above, their corresponding single- and multi-reference configuration interaction (CI) methods are also available for use in our codes. We also remark that all the implemented methods have been parallelized utilizing both shared- and distributed-memory parallelism to speed up the execution times.

III. BENCHMARK CALCULATIONS

As a first application of the new relativistic code, we have performed benchmark calculations for the total energies, equilibrium bond lengths, and vibrational frequencies of the monoxides of Group IVa, such as, CO, SiO, GeO, SnO, and PbO. Since relativistic CCSD and CCSD(T) codes were previously available[11,12] and the effect of relativity on the correlation contributions of up to perturbative triple excitations were also studied,[66–68] we have focused on the iterative triples and the quadruples increments [i.e., CCSDT-CCSD(T), CCSDT(Q)-CCSDT, and CCSDTQ-CCSDT(Q)] in the current work. These contributions were found to be essential for light atoms and molecules for high-accuracy calculations.[84–90]

We, therefore, have evaluated the contributions of iterative triple and quadruple excitations using the double- and triple-zeta quality basis sets as the standard practice followed in high-accuracy calculations. The basis sets used in our calculations include the correlation consistent polarized core-valence double zeta (cc-pCVDZ) and triple zeta (cc-pCVTZ) basis sets of Dunning and co-workers[91,92] for the light atoms such as C, O, and Si, and Dyall basis sets[93,94] of similar quality for heavier atoms such as Ge, Sn, and Pb. All these basis sets are available in the recent version of the DIRAC suite itself. The relativistic basis sets given by Dyall are uncontracted whereas the nonrelativistic Dunning basis sets are contracted.

In order to be consistent, we have uncontracted the Dunning basis sets in our calculations, for both relativistic and nonrelativistic cases alike. The use of uncontracted basis sets especially for the diatomic molecules involving Sn and Pb in the triple-zeta calculations require large computational resources and long execution times. In addition, the number of small component basis functions generated using the kinetic balance condition will become too large, and considering the two electron integrals involving them becomes a burden. Hence, we have used an approximation proposed by Visscher[95] in which the two electron integral contributions from the small–small (SS) components are neglected in the coupled cluster calculation. To obtain reliable total energies we did, however, also run Hartree–Fock calculations in which the SS integrals are included, yielding a correction that is included in the reported coupled cluster energy. This simple scheme (similar to the $^4DCG^*$ scheme discussed by Sikkema *et al.*[96]) reduces the computational time and the memory requirements of the calculations significantly with negligible loss of accuracy.

Guided by the observations reported in Ref. 97, we have frozen the noble gas core and the highest-lying d shell electrons in the DZ basis sets, that is, we have only correlated the $2s$ and $2p$ electrons of oxygen and the ns and np electrons of the Group IVa elements, altogether 10 electrons, in order to reduce the computational costs further. In the TZ basis set the last occupied d shell electrons of the heavy atoms were also correlated in the post-SCF calculations, which amounts to correlating 20 electrons for GeO, SnO, and PbO. For the CO and SiO molecules, to keep the number of correlated electrons more or less constant and to perform as complete calculations as possible, no electrons were frozen for CO and only the $1s$ electrons of O and Si were frozen for SiO. This results in 14 and 18 correlated electrons for CO and SiO, respectively. During the core freezing the identification of the d shell orbitals of the heavy atoms and the $2s$ orbitals of oxygen does not pose any challenge for molecules up to SnO as they are well separated and no orbital mixing is seen. However, for PbO the selection of the core orbitals for freezing is less straightforward as the oxygen $2s$ orbitals mix significantly with the $5d$ orbitals of Pb, and hence, there are a few molecular orbitals with significant $2s$ character. In this particular case we have frozen the ones with the lower orbital energy. Further, we have also set a maximum energy threshold for the high-lying virtuals in DZ and TZ calculations to be 5 E_h and 10 E_h, respectively. Adhering to these limitations, we have performed CC calculations up to CCSDTQ and CCSDT in DZ and TZ basis, respectively.

A series of test calculations have been performed for SiO to assess the accuracy of the results in view of the limitations considered above viz. freezing of the inner core electrons and truncation of higher virtual orbitals in the DZ basis. The CCSD energy with the full basis set is obtained to be -365.09 E_h where as freezing the noble gas cores of both Si and O, that is, freezing $n = 2$ shell for Si and $n = 1$ shell for O yields a CCSD energy of -364.77 E_h. Hence, the frozen noble gas core approximation overestimates the CCSD energy by 0.32 E_h. The truncation of higher virtuals above the threshold energy of 5 E_h results in an overestimation of 0.02 E_h. Therefore, the total deviation of the energy from its original value is 0.34 E_h for SiO in the DZ basis at the CCSD level of the theory due to the approximations considered above. This would be even more significant for larger molecules and for larger basis sets, however, our main aim in the current work is to compute the higher-order correlation contributions to the total energies and other spectroscopic properties and not the absolute values themselves, and also much of the error caused by the above constraints is supposed to cancel in the higher order calculations.

A Gaussian charge distribution for the nucleus has been considered in the relativistic calculations, while, a point charge distribution has been used in the nonrelativistic calculations. However, the basis sets, geometries, symmetry groups used in both calculations are exactly the same. The exponents used for the Gaussian distribution of nuclear charge are 680775029.29, 586314366.55, 434677488.23, 252356133.99, 190677181.54, and 137688400.81 for C, O, Si, Ge, Sn, and Pb, respectively. We would like to remark that the nonrelativistic test calculations using a Gaussian charge distribution instead of a point charge distribution showed only negligible change in the results of bond lengths and vibrational frequencies.

The total energies for the diatomic molecules considered in this work have been calculated at the respective experimental equilibrium bond lengths (r_e) taken from Ref. 98, which (in Å) are 1.128323, 1.509739, 1.624648, 1.832505, and 1.921813 for CO, SiO, GeO, SnO, and PbO, respectively. In order to calculate spectroscopic parameters such as the equilibrium geometry and the vibrational frequencies, four additional energy calculations have been carried out at four points around r_e with the separation $(r - r_e)$ of ± 0.02 Å and ± 0.04 Å, and second-order polynomials have been fitted to the resulting points on the potential energy curves. The harmonic frequencies are calculated for the most abundant isotopes of the elements considered viz. C^{12}, O^{16}, Si^{28}, Ge^{74}, Sn^{120}, and Pb^{208}, whose nuclear masses (in amu) are, 12.0, 15.99491, 27.97693, 73.92117, 119.90219, and 207.97665, respectively, which are taken from Ref. 99.

The relativistic calculations have been performed using the recently developed version of the MRCC program[59] and its interface to the local version of the DIRAC08 program,[60] whereas the nonrelativistic calculations have been performed using the CFOUR program[100] and its interface to MRCC program developed earlier. These two seamless interfaces enable us to perform higher-order relativistic and nonrelativistic correlation calculations, respectively.

We should emphasize at this point that the results, especially those for quadruple excitations should be treated with some caution because of the small number of correlated electrons and the small basis sets. The DZ basis set itself is rather small, and the quality of the one-electron basis is further worsened by the truncation of the virtual space. Furthermore, since the oxygen atom bears a partial negative charge in the heavier molecules, the use of augmented basis sets for oxygen would be desirable for a quantitative description. Nevertheless, our intention was to gain some insight into the behavior of higher-order correlation contributions for heavier element, and CC calculations including up to quadruple excitations

are currently hardly possible with a larger number of basis functions. Thus we think that our conclusions are not definitive, but still instructive for high-accuracy calculations.

IV. RESULTS AND DISCUSSION

The calculated results of the total energies, equilibrium bond lengths, and harmonic vibrational frequencies together with the relativistic and higher-order correlation contributions for the Group IVa monoxides are presented in Tables I–III, respectively. In columns four and five, the relativistic and nonrelativistic quantities are presented, respectively, at different levels of the CC theory, both in DZ and TZ basis sets. The relativistic contribution, i.e., the difference between columns four and five is shown in column six for each level of the theory for all the quantities of interest. The behavior of the single-reference CC methods used in these calculations can be studied with the aid of columns seven and eight in which the difference between the given and the preceding level of the theory is looked at in relativistic and nonrelativistic cases, respectively. The column nine in the tables gives the significance of relativistic effects in the hierarchy of CC methods.

We would like to emphasize that the correlation contributions higher than the perturbative triples [i.e., CCSD(T)] are highlighted in the current paper. The contributions of the iterative triples [i.e., CCSDT] have been studied in the TZ basis and the quadruples have been studied in the DZ basis. Before discussing the observed trends, we introduce a terminology to be used hereafter. The correlation contribution due to partial triples [i.e., CCSD(T)-CCSD] will henceforth be referred to as (T)-contribution, [CCSDT-CCSD(T)] will be referred to as T-contribution, and the similar terminology follows for (Q)- and Q-contributions. The total correlation contributions of triples and quadruples (i.e., [(T) + T] and [(Q) + Q]) are presented in columns 10 and 11, respectively, and the relative contribution of the perturbative approximations over the total triples and quadruples contributions for both relativistic and nonrelativistic cases are shown in the last two columns of Tables I–III.

In this work besides observing that the total energies in the relativistic case are much lower compared to their respective nonrelativistic energies, as is well known in the literature, we observe the contraction of bond lengths and the reduction in the vibrational frequencies in the diatomic molecules studied due to the inclusion of the relativistic effects. The magnitude of the relativistic contribution to the total energy monotonically increases from 0.1 E_h for CO to 1389.8 E_h for PbO. The contraction of bond length varies from 0.0002 Å for CO to 0.0306 Å for PbO, similarly, the change in the vibrational frequencies falls in the range of 2 cm^{-1} for CO to 81 cm^{-1} for PbO due to the influence of relativistic effects.

In the following three subsections we will discuss the trends observed in the calculations of total energies, equilibrium molecular geometries, and harmonic vibrational frequencies separately due to the inclusion of relativistic and higher-order correlation effects in detail. In the last subsection, we will summarize our findings for each molecule considered in this work individually and compare our results with the available calculations.

A. Total energies

The total energies for the diatomic molecules are presented in Table I. From the table, we observe that the entire quadruples contribution is an order of magnitude smaller than the entire triples contribution in the DZ basis for both relativistic and nonrelativistic cases alike. This factor is in consistent with the previously reported observations in the nonrelativistic calculations by Kállay *et al.*[45] Furthermore, the ratio of [(Q)/Q] contributions is 10 for CO and five for SiO both in relativistic and nonrelativistic cases, in line with the previous nonrelativistic calculations.[69] The difference in the higher-order correlation contributions between the relativistic and nonrelativistic cases in the DZ basis are very small for all the molecules but PbO (for which the SO-coupling effects lead to qualitative changes in the bonding between the atoms). The ability of the (T) approximation to describe the effect of triple excitations does show some dependence on the basis set. For the DZ basis we see that for the lighter molecules the (T) approximation recovers about 95% of the full triples contribution, both in the relativistic and the nonrelativistic case. For PbO the T-contribution is unimportant in the nonrelativistic calculation, while in the relativistic case the T-contribution is clearly larger than for the lighter elements. In the TZ-basis such differences between the nonrelativistic and relativistic correlation contributions are less prominent and the relative importance of the T-contribution is also smaller.

In the heavier molecules, SnO and PbO the convergence with excitation level is less quick in both relativistic and nonrelativistic calculations. This is probably caused by the close-lying occupied and virtual orbitals, which make the molecules somewhat multireference in nature. Another explanation is possibly the limited amount of the higher angular momentum functions in the DZ basis of Sn and Pb, which makes the correlation treatment vulnerable to basis set incompleteness errors.

Looking at the magnitudes of the relativistic contributions to T-contributions we conclude that up to the third row of the periodic table the nonrelativistic calculations will suffice for the iterative triples, while from fourth row onward the inclusion of relativistic effects may be necessary if one is seeking an accuracy of ~1 kJ/mol. For SnO and PbO the Q-contribution is larger than the T-contribution, particularly, in the nonrelativistic case, indicating the importance of higher excitations for heavy elements. It is interesting to note that the CCSD(T) result in the nonrelativistic case of PbO is closer to the CCSDT result and does not exhibit the erratic behavior of the perturbative quadruples approach. The noticeable observation that the relativistic effects have negligible influence on the (Q)- and Q-contributions for molecules up to SnO suggests that one can safely perform nonrelativistic calculations for quadruples up to fourth row, however, fifth row elements need to be treated relativistically both for the perturbative and full quadruples contributions. Nevertheless, from the third row the use of the CCSDT(Q) method is not recommended,

TABLE I. Total energies and correlation contributions to total energies for the oxides of Group IVa (in E_h).

Molecule	Basis set	Method	Total energy			Correlation contribution[a]			[(T)+T] and [(Q)+Q] contribution		% covered by pert. theory	
			Rel.	Nonrel.	Diff.	Rel.	Nonrel.	Diff.	Rel.	Nonrel.	Rel.	Nonrel
CO	DZ	CCSD	–113.116892	–113.045396	–0.071497	–	–	–				
		CCSD(T)	–113.127776	–113.056271	–0.071506	–0.010884	–0.010875	–0.000009				
		CCSDT	–113.128305	–113.056800	–0.071505	–0.000529	–0.000530	0.000001	–0.011413	–0.011405	95	95
		CCSDT(Q)	–113.129320	–113.057812	–0.071507	–0.001014	–0.001012	–0.000002				
		CCSDTQ	–113.129221	–113.057714	–0.071507	0.000098	0.000098	0.000000	–0.000916	–0.000914	111	111
	TZ	CCSD	–113.234331	–113.162680	–0.071651	–	–	–				
		CCSD(T)	–113.251421	–113.179755	–0.071667	–0.017090	–0.017075	–0.000015				
		CCSDT	–113.251648	–113.179984	–0.071665	–0.000227	–0.000229	0.000002	–0.017317	–0.017304	99	99
SiO	DZ	CCSD	–364.748319	–364.067793	–0.680526	–	–	–	673			
		CCSD(T)	–364.759823	–364.079278	–0.680545	–0.011504	–0.011485	–0.000019				
		CCSDT	–364.760658	–364.080114	–0.680545	–0.000835	–0.000836	0.000000	–0.012339	–0.012320	93	93
		CCSDT(Q)	–364.762136	–364.081588	–0.680548	–0.001477	–0.001475	–0.000003				
		CCSDTQ	–364.761862	–364.081315	–0.680547	0.000274	0.000273	0.000001	–0.001203	–0.001201	123	123
	TZ	CCSD	–365.006032	–364.324667	–0.681365	–	–	–				
		CCSD(T)	–365.025192	–364.343796	–0.681396	–0.019160	–0.019129	–0.000031				
		CCSDT	–365.025486	–364.344094	–0.681391	–0.000294	–0.000298	0.000005	–0.019454	–0.019427	98	98
GeO	DZ	CCSD	–2172.692427	–2150.518030	–22.174396	–	–	–				
		CCSD(T)	–2172.706184	–2150.531709	–22.174474	–0.013757	–0.013679	–0.000078				
		CCSDT	–2172.707037	–2150.532564	–22.174473	–0.000854	–0.000854	0.000001	–0.014610	–0.014533	94	94
		CCSDT(Q)	–2172.709015	–2150.534533	–22.174481	–0.001978	–0.001970	–0.000008				
		CCSDTQ	–2172.708548	–2150.534072	–22.174476	0.000467	0.000461	0.000006	–0.001511	–0.001509	131	131
	TZ	CCSD	–2173.135076	–2150.946760	–22.188316	–	–	–				
		CCSD(T)	–2173.161189	–2150.972528	–22.188661	–0.026113	–0.025768	–0.000345				
		CCSDT	–2173.160952	–2150.972330	–22.188622	0.000237	0.000197	0.000040	–0.025876	–0.025571	101	101
SnO	DZ	CCSD	–6251.307990	–6098.050245	–153.257745	–	–	–				
		CCSD(T)	–6251.324415	–6098.066577	–153.257838	–0.016425	–0.016332	–0.000093				
		CCSDT	–6251.325177	–6098.067348	–153.257829	–0.000762	–0.000771	0.000009	–0.017187	–0.017103	96	95
		CCSDT(Q)	–6251.328121	–6098.070297	–153.257824	–0.002945	–0.002949	0.000004				
		CCSDTQ	–6251.327165	–6098.069361	–153.257805	0.000956	0.000936	0.000020	–0.001989	–0.002013	148	147
	TZ	CCSD	–6251.817765	–6098.545097	–153.272669	–	–	–				
		CCSD(T)	–6251.852469	–6098.579002	–153.273467	–0.034704	–0.033905	–0.000798				
		CCSDT	–6251.851561	–6098.578226	–153.273336	0.000907	0.000776	0.000131	–0.033796	–0.033129	103	102
PbO	DZ	CCSD	–20988.847133	–19599.038825	–1389.808308	–	–	–				
		CCSD(T)	–20988.862163	–19599.055232	–1389.806931	–0.015030	–0.016407	0.001377				
		CCSDT	–20988.863734	–19599.055486	–1389.808248	–0.001571	–0.000254	–0.001318	–0.016601	–0.016661	91	98
		CCSDT(Q)	–20988.866576	–19599.058371	–1389.808205	–0.002841	–0.002884	0.000043				
		CCSDTQ	–20988.865317	–19599.057377	–1389.807940	0.001259	0.000994	0.000265	–0.001582	–0.001890	180	153
	TZ	CCSD	–20989.357710	–19599.558559	–1389.799151	–	–	–				
		CCSD(T)	–20989.393339	–19599.593526	–1389.799812	–0.035629	–0.034968	–0.000661				
		CCSDT	–20989.392541	–19599.592633	–1389.799908	0.000798	0.000894	–0.000096	–0.034831	–0.034074	102	103

[a]Difference between the total energies obtained with the given method and the preceding method.

and the parent CCSDTQ approach should be employed for the estimation of quadruples effects.

B. Molecular geometries

The relativistic contraction of the bond lengths has been observed uniformly for all those molecules studied in this work. This is concurrent to the observations made in the case of dihalogens.[67] An unexpected bond elongation seen only in the DZ basis in SnO is in contradiction with the bond contraction observed in the TZ basis in the same system. This spurious result was suspected to be due to the omission of 4*d* electrons in the correlation calculations. In order to verify this, we performed a test calculation correlating 10 electrons in the TZ basis and observed indeed a similar bond elongation of 0.00579 Å in the CCSD and 0.00737 Å in the CCSD(T) case. A further calculation performed using 20 correlated electrons, instead of 10, in the DZ basis showed a bond contraction of 0.00661 Å and 0.00569 Å for CCSD and CCSD(T), respectively. This suggests that inclusion of 4*d* electrons in the correlation calculations are necessary for getting the correct results for SnO. Unfortunately, however, it is rather difficult to perform the quadruples calculations in the DZ basis with 20 correlated electrons within the resources available for us. Nevertheless, the absence of similar observation (i.e., bond elongation) in the results of the DZ basis with 10 correlated electrons for PbO is intriguing.

The (T)-contribution in the TZ basis is larger than a factor of 100 over the T-contribution for all molecules down the group except PbO. For PbO this factor is a mere 4 in the relativistic case and 26 in the nonrelativistic case. In addition, the sign of the T-contribution in the relativistic case in PbO is opposite to the sign observed in all other cases. These results are less easy to rationalize than the trends observed above in the correlation energy as they result from a combination of relativistic effects on the correlation and the usual bond weakening (caused by spin-orbit coupling) and bond contraction (caused by the scalar relativistic effects that shrink the valence p-orbitals) trends. The increasing differences between nonrelativistic and relativistic results do, however, illustrate the need to treat relativity and electron correlation simultaneously.

The correlation contributions due to the entire triples in the DZ basis are at least a factor of 6 larger than those for the entire quadruples. This trend is observed to be the same in both relativistic and nonrelativistic cases uniformly across the entire group. The ratio of perturbative and iterative quadruples contributions [i.e., (Q)/Q] decreases monotonically down the group and again the performance of CCSDT(Q) is rather poor from the third row onward in both relativistic and nonrelativistic cases. The relativistic effects to the triples and quadruples are significant for SnO and PbO only. Further, the relativistic contribution to (Q) in the case of PbO shows a negative sign breaking the general trend observed in all other molecules of the group.

The underlying conclusion of Table II is that the inclusion of the relativistic effects is necessary in the hierarchy of higher-order correlation calculations, in particular, full triples, and quadruples for SnO and PbO. However, for lighter molecules the nonrelativistic methods are recommended for the higher-order correlation calculations unless one is interested in the change in the bond lengths of less than 0.00005 Å.

C. Harmonic frequencies

The harmonic frequencies are lower in the relativistic case in comparison to the nonrelativistic case for the Group IVa monoxides. This is in agreement to the trends observed for dihalogens[67] and interhalogens[66] by Visscher *et al.*, and is mainly due to the spin-orbit coupling that mixes in antibonding contributions, thus weakening the formal triple bond of the Group IVa monoxides.[65]

The correlation contribution to (both perturbative and iterative) triples appears to be approximately same in both the relativistic and the nonrelativistic cases in the TZ basis for light molecules up to GeO. However, for SnO and PbO this trend is quite different. The T-contribution in the relativistic case is noticeably smaller than that in the nonrelativistic case for SnO. The (T)- and T-contributions show opposite signs in PbO, particularly in the relativistic case, breaking the trend exhibited by other molecules in the TZ basis. The T-contribution is unusually large in the relativistic case for PbO making the ratio [(T)/T] to be ~2 unlike in other molecules in which this ratio is more than 10 in the TZ basis. In the nonrelativistic case this ratio is ~4 for PbO. From our results it can be inferred that the CCSDT(Q) approach performs very poorly in the vibrational frequency calculations, both in relativistic and nonrelativistic cases, in almost all the molecules of current interest.

No particular trend has been displayed in the relativistic contribution to correlation increments for frequencies shown in column nine in Table III. However, it is certainly clear that the relativistic contributions to T-, (Q)-, and Q-increments are negligibly small for elements up to fourth row. For PbO the T-contribution is significantly large with a value of about -8 cm^{-1} in the TZ basis and -18 cm^{-1} in the DZ basis. The Q-contribution in PbO is also large and is comparable to the T-contribution and hence, one needs to consider the relativistic effects for full quadruples also.

D. The individual molecules

Below we shall discuss some noteworthy features for each individual molecule treated in this work.

1. CO

The relativistic contributions for the total energies of CO are about 0.07 E_h. A small contraction in the bond length of (~0.0002 Å) and a decrease in the vibrational frequency of (2 cm^{-1}) has been observed due to the inclusion of relativistic effects. It is interesting to observe that the influence of the relativistic effects in shortening the bond length and in decreasing the vibrational frequency of CO molecule is constant throughout the hierarchy of correlation methods considered. Further, the correlation contributions appear to be the same

TABLE II. Equilibrium bond lengths and the correlation contributions to the equilibrium bond lengths for the oxides of Group IVa (in Å).

	Basis		Bond length			Correlation contribution[a]			[(T)+T] and [(Q)+Q] contribution		% covered by pert. theory	
Molecule	set	Method	Rel.	Nonrel.	Diff.	Rel.	Nonrel.	Diff.	Rel.	Nonrel.	Rel.	Nonrel
CO	DZ	CCSD	1.13409	1.13426	–0.00017	–	–	–				
		CCSD(T)	1.13975	1.13990	–0.00016	0.00566	0.00564	0.00002				
		CCSDT	1.14004	1.14020	–0.00016	0.00029	0.00029	0.00000	0.00595	0.00594	95	95
		CCSDT(Q)	1.14075	1.14090	–0.00015	0.00071	0.00071	0.00000				
		CCSDTQ	1.14060	1.14076	–0.00016	–0.00015	–0.00015	0.00000	0.00056	0.00056	127	126
	TZ	CCSD	1.12796	1.12816	–0.00020	–	–	–				
		CCSD(T)	1.13478	1.13496	–0.00018	0.00682	0.00680	0.00002				
		CCSDT	1.13475	1.13493	–0.00018	–0.00004	–0.00003	0.00000	0.00679	0.00677	101	100
SiO	DZ	CCSD	1.53537	1.53565	–0.00029	–	–	–				
		CCSD(T)	1.54553	1.54575	–0.00023	0.01016	0.01010	0.00006				
		CCSDT	1.54609	1.54631	–0.00022	0.00056	0.00056	0.00001	0.01073	0.01066	95	95
		CCSDT(Q)	1.54824	1.54846	–0.00021	0.00215	0.00214	0.00000				
		CCSDTQ	1.54746	1.54768	–0.00023	–0.00078	–0.00077	–0.00001	0.00136	0.00137	157	156
	TZ	CCSD	1.50929	1.50962	–0.00033	–	–	–				
		CCSD(T)	1.52010	1.52036	–0.00026	0.01081	0.01075	0.00006				
		CCSDT	1.52000	1.52027	–0.00027	–0.00010	–0.00010	–0.00001	0.01071	0.01065	101	101
GeO	DZ	CCSD	1.62617	1.62773	–0.00155	–	–	–				
		CCSD(T)	1.64040	1.64161	–0.00121	0.01422	0.01388	0.00034				
		CCSDT	1.64104	1.64219	–0.00116	0.00064	0.00059	0.00005	0.01486	0.01447	96	96
		CCSDT(Q)	1.64433	1.64544	–0.00111	0.00329	0.00325	0.00004				
		CCSDTQ	1.64300	1.64413	–0.00113	–0.00133	–0.00131	–0.00002	0.00196	0.00194	168	168
	TZ	CCSD	1.61312	1.61638	–0.00327	–	–	–				
		CCSD(T)	1.62800	1.63085	–0.00285	0.01488	0.01446	0.00042				
		CCSDT	1.62784	1.63069	–0.00285	–0.00016	–0.00015	0.00000	0.01473	0.01431	101	101
SnO	DZ	CCSD	1.85162	1.84958	0.00204	–	–	–				
		CCSD(T)	1.87334	1.87025	0.00309	0.02172	0.02067	0.00105				
		CCSDT	1.87355	1.86991	0.00364	0.00021	–0.00034	0.00055	0.02193	0.02033	99	102
		CCSDT(Q)	1.88133	1.87705	0.00428	0.00778	0.00714	0.00064				
		CCSDTQ	1.87733	1.87345	0.00388	–0.00401	–0.00361	–0.00040	0.00377	0.00353	206	202
	TZ	CCSD	1.81471	1.82237	–0.00766	–	–	–				
		CCSD(T)	1.83569	1.84228	–0.00659	0.02098	0.01990	0.00108				
		CCSDT	1.83554	1.84198	–0.00644	–0.00015	–0.00030	0.00015	0.02083	0.01960	101	102
PbO	DZ	CCSD	1.91373	1.92827	–0.01454	–	–	–				
		CCSD(T)	1.92364	1.95427	–0.03063	0.00991	0.02600	–0.01609				
		CCSDT	1.93219	1.95186	–0.01967	0.00855	–0.00241	0.01096	0.01845	0.02359	54	110
		CCSDT(Q)	1.94098	1.96108	–0.02011	0.00879	0.00923	–0.00044				
		CCSDTQ	1.93494	1.95627	–0.02133	–0.00604	–0.00481	–0.00123	0.00275	0.00442	319	209
	TZ	CCSD	1.90265	1.91845	–0.01580	–	–	–				
		CCSD(T)	1.91933	1.94136	–0.02203	0.01668	0.02291	–0.00623				
		CCSDT	1.92367	1.94046	–0.01679	0.00434	–0.00090	0.00524	0.02102	0.02201	79	104

[a]Difference between the bond lengths obtained with the given method and the preceding method.

TABLE III. Harmonic frequencies and the correlation contributions to the harmonic frequencies for the oxides of Group IVa (in cm^{-1}).

	Basis		Harmonic frequency			Correlation contribution[a]			[(T)+T] and [(Q)+Q] contribution		% covered by pert. theory	
Molecule	set	Method	Rel.	Nonrel.	Diff.	Rel.	Nonrel.	Diff.	Rel.	Nonrel.	Rel.	Nonrel.
CO	DZ	CCSD	2024	2026	–2	–	–	–				
		CCSD(T)	2009	2011	–2	–15	–15	0				
		CCSDT	2008	2010	–2	–1	–1	0	–16	–16	94	95
		CCSDT(Q)	2006	2008	–2	–2	–2	0				
		CCSDTQ	2007	2009	–2	1	1	0	–1	–1	177	156
	TZ	CCSD	2009	2011	–2	–	–	–				
		CCSD(T)	1994	1997	–2	–14	–14	0				
		CCSDT	1995	1997	–2	0	0	0	–14	–14	103	103
SiO	DZ	CCSD	1107	1110	–2	–	–	–				
		CCSD(T)	1093	1096	–2	–14	–14	0				
		CCSDT	1093	1095	–2	0	0	0	–14	–14	99	99
		CCSDT(Q)	1089	1092	–2	–3	–4	0				
		CCSDTQ	1091	1094	–2	2	2	0	–2	–2	211	195
	TZ	CCSD	1094	1096	–2	–	–	–				
		CCSD(T)	1082	1085	–2	–12	–12	0				
		CCSDT	1083	1085	–2	1	0	0	–11	–11	106	104
GeO	DZ	CCSD	839	846	–7	–	–	–				
		CCSD(T)	826	832	–7	–13	–13	0				
		CCSDT	826	833	–7	1	1	0	–13	–12	104	106
		CCSDT(Q)	822	828	–7	–5	–5	0				
		CCSDTQ	824	831	–7	3	3	0	–2	–2	219	214
	TZ	CCSD	810	820	–10	–	–	–				
		CCSD(T)	798	808	–10	–12	–12	0				
		CCSDT	799	809	–10	1	1	0	–11	–11	106	106
SnO	DZ	CCSD	703	725	–22	–	–	–				
		CCSD(T)	691	711	–20	–13	–14	2				
		CCSDT	692	714	–21	1	3	–1	–11	–11	112	124
		CCSDT(Q)	684	705	–21	–8	–8	0				
		CCSDTQ	689	711	–21	6	6	0	–3	–3	307	287
	TZ	CCSD	663	683	–20	–	–	–				
		CCSD(T)	652	671	–19	–12	–13	1				
		CCSDT	653	673	–20	1	2	–1	–11	–11	111	117
PbO	DZ	CCSD	565	647	–81	–	–	–				
		CCSD(T)	598	630	–33	32	–17	49				
		CCSDT	580	635	–56	–18	5	–23	14	–12	226	141
		CCSDT(Q)	572	625	–53	–8	–11	3				
		CCSDTQ	569	631	–62	–3	7	–10	–11	–4	72	279
	TZ	CCSD	555	630	–75	–	–	–				
		CCSD(T)	572	617	–46	17	–13	30				
		CCSDT	564	620	–56	–8	3	–11	9	–10	185	129

[a]Difference between the harmonic frequencies obtained with the given method and the preceding method.

for both relativistic and nonrelativistic cases at each level of the correlation theory. For a light neutral molecule like CO one can therefore safely ignore the relativistic effects in the higher-order correlation contributions.

2. SiO

SiO being heavier than CO, shows an energy decrease of about 0.68 E_h while going from the nonrelativistic to the relativistic case which is an order of magnitude larger than the relativistic effect observed in CO. The influence of the relativistic effects lead to a decrease in the bond length in the range ~0.0002–0.0003 Å, and a decrease in the frequency of about 2 cm^{-1}. The relativistic contributions to the higher-order correlation effects are insignificant for SiO and they can be omitted unless one is looking for completeness in the calculations.

3. GeO

The relativistic effects begin to appreciably influence the total energy of the diatomic molecules starting from GeO in the monoxide series considered in this work with a contribution of ~ 22 E_h which, however, is a mere ~1% of the total value. The bond length contraction of 0.001–0.002 Å in the DZ basis and 0.003 Å in the TZ basis is consistently observed for GeO at different levels of correlation theory. A bond contraction of 0.003 Å has also been observed by Dyall[65] in an uncorrelated DHF calculation. The relativistic decrease in the vibrational frequency varies from ~7 cm^{-1} in DZ basis to ~10 cm^{-1} in TZ basis. The observed change in the frequency in the DHF calculation by Dyall[65] is 2(3) times smaller than the one observed by us in the DZ(TZ) basis, which may be due to the inclusion of electron correlation in our calculations, or due to the difference in basis set. We would like to recall that we have used optimized relativistic basis sets of Dyall for Ge unlike the case for CO and SiO for which we have used Dunning basis sets. Since GeO stands in the border line between the relativistic and the nonrelativistic domains, we recommend to treat the higher-order correlation effects together with the relativistic effects in GeO, if a high accuracy is needed.

4. SnO

The relativistic effects get more pronounced for heavier molecules such as SnO with contributions of 153.3 E_h which is ~2.5% to its total energy. SnO shows a bond elongation of about 0.002–0.004 Å in the DZ basis in contrast to the bond contraction observed for all other molecules studied in this work. However, in the TZ basis we see a strong bond contraction of about 0.006–0.008 Å as anticipated. The latter bond length contraction compares well with both the uncorrelated DHF results (0.007 Å) of Dyall[65] and the correlated scalar relativistic DKH5 results (0.004 Å) of Wolf *et al.*[64] The reasons for the observed discrepancy in the change in bond length between the DZ and TZ calculations are discussed in Sec. IV B.

The relativistic contribution to the harmonic frequencies varies from −20 to −22 cm^{-1} at different levels of correlation theory in the DZ basis and falls in the range −19 to −20 cm^{-1} in the TZ basis. In comparison with the above-mentioned calculations of Dyall and Wolf *et al.* the decrease of the frequency is about twice as large, which can be understood from the lack of correlation in the calculations by Dyall and the lack of spin-orbit coupling in the calculations by Wolf *et al.*, both of which will weaken the bond by mixing in antibonding orbitals. The inclusion of relativistic effects in the higher-order correlation calculations is certainly recommended.

5. PbO

The relativistic contribution to the total energy of PbO is ~1390 E_h, which is ~7% of its total energy. A bond contraction of 0.01–0.03 Å has been observed for PbO at different correlation levels of the theory. The relativistic bond contraction being larger at the CCSD(T) level than that at the CCSD level sets an unusual trend for PbO. The decrease in the bond distance for PbO observed earlier by Iliaš *et al.*[82] with the DC and Barysz–Sadlej–Snijders (BSS) Hamiltonians in conjunction with the CCSD(T) approach (0.003 Å), as well as by Lenthe *et al.*[101] using the ZORA approach (0.002 Å) are approximately an order of magnitude smaller than that observed in this work, which can be ascribed as due to the lack of spin-orbit coupling terms. The SO corrected CCSD(T) result of Metz *et al.*,[102] as quoted in Ref. 101 is 0.037 Å, which is more or less in agreement with our result. The DHF results of Dyall[65] show a bond length contraction of 0.0146 Å.

The relativistic decrease in the harmonic vibrational frequency is 33–81 cm^{-1} in the DZ basis and 46–75 cm^{-1} in the TZ basis. In the aforementioned calculations by Iliaš *et al.* and by Lenthe *et al.* approximately 10 cm^{-1}, while around 44 cm^{-1} by Metz *et al.*, and 88 cm^{-1} by Dyall has been observed as the change in the frequency due to relativistic effects. The latter two results are more or less in agreement with the present calculations. The decrease in the frequency at the CCSD level is observed to be unusually large when compared to that at the higher levels of correlation theory. On the other hand, the harmonic frequency seems to be overestimated with the CCSD(T) approach, in particular, in the relativistic case and at the higher levels of the correlation theory it decreases slowly. It is also observed that the ratio of the relativistic contributions to CCSD and CCSD(T) results in the DZ basis in PbO is ~3 as against a ratio of ~1 observed in other molecules. Despite the trends being different, it is undoubtedly clear that the relativistic effects have strong influence on the higher-order correlation effects in SnO and PbO.

V. CONCLUDING REMARKS

The development of a general order relativistic CC code has been reported based on Kramers-paired molecular spinors, double group symmetry, and the full Dirac–Coulomb as well as several approximate relativistic Hamiltonians. The new program is useful for benchmarking lower-level relativistic correlation methods. Further, it also unfolds the way for

high precision calculations for systems where the relativistic effects, in particular, the spin-orbit coupling are strong, and a rigorous treatment of the relativity is required.

Benchmark calculations have been performed for the total energies, bond lengths, and vibrational frequencies of the oxides of Group IVa. The behavior of the relativistic contributions with increasing level of correlation and atomic number has been monitored with special regard to iterative triples as well as quadruples contributions. Our results suggest that up to the third (fourth) row of the periodic table the iterative triples contributions for total energies and bond lengths (harmonic frequencies) can be calculated using the nonrelativistic CC methods, and the explicit inclusion of relativity is only required from the fourth (fifth) row. The contribution of quadruple excitations in the case of total energies and geometries can be evaluated by nonrelativistic approaches up to fourth- and third-row molecules, respectively, and a full relativistic treatment is only necessary for heavier elements. For harmonic frequencies the inclusion of relativity for the calculation of quadruples corrections is only necessary for the fifth row. The performance of the CCSDT(Q) method does not seem to be satisfactory from the third row onwards for any of the considered properties, and thus, the use of the full CCSDTQ method is recommended. We note again that there exists some caveat concerning our conclusions especially for quadruple excitations because of the small basis sets used, nevertheless these calculations can be considered as state-of-the-art, and larger calculations are not feasible in the near future.

We would like to remark that in the current calculations, the relativistic correction to the Coulomb interaction called Breit interaction is not included. Since these contributions may be important in the high accuracy calculations, we will consider including them in the future. In addition, in order to effectively handle open-shell systems, we plan to consider implementing either a fully unrestricted spinor optimization followed by MO transformation or the semi-canonical orbital option in the future work.

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